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Scanning tunneling microscopy and spectroscopy of palladium clusters supported on graphite

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The surface of palladium clusters supported on graphite has been investigated with a scanning tunneling microscope in ultrahigh vacuum. Electron tunneling spectra were measured for clusters of different sizes. The surface density of electronic states at the Fermi energy presents a strong size dependence for small clusters and becomes size independent for clusters larger than a critical volume. This phenomenon has been interpreted in terms of the size-dependent electronic structure of the particles.

I. INTRODUCTION

Small metallic particles exhibit physical and chemical properties that are intermediate between those of a molecule and a solid.[1] The electronic structure of the small aggregate is determined by the confinement of the electrons in a zero-dimensional mesoscopic structure, and strongly depends on the size and on the structure of the surface. Alkali-metal clusters have been extensively investigated with supersonic-jet machines,[2] designed for the production and size selection of free particles. The discovery of the magic numbers, namely highly stable structures determined by the closure of an electronic shell, represented an important step in the comprehension of the properties of the microaggregates. Besides this fundamental interest, the numerous and important applications of cluster-based materials in chemistry (heterogeneous catalysis),[3] optics (nonlinear optical devices) (Ref. 4), and microelectronics (single-electron nanodevices) (Ref. 5) are now driving the interest of the researchers towards transition-metal particles and their interaction with the external environment (namely the support or the embedding medium), which determines, to a large extent, the properties and the structure of the particles.

The unavoidable size distribution of the metallic particles in the samples is the basic problem for any spectroscopic approach, as the size effects are averaged over the ensemble of sizes. As shown by Kubo *et al.*,[6] the properties of an ensemble of particles are determined by the statistics of the energy levels, which can be described in terms of random Hamiltonians. Devaty and Sievers[7] demonstrated that the effects of the discretization of the electronic structure of the single particles are completely washed out in the dielectric function of a composite material containing metal clusters with a log-normal size distribution characterized by $\sigma \geq 1.1$. In order to overcome this problem, several techniques have been developed for the size selection of the aggregates before the deposition onto a support or in an embedding dielectric. Recently, Schmid *et al.* succeeded in producing consistent amounts of identical clusters, selected and stabilized by ligands on the surface of the particles.[8] However, the molecules that are chemically bound to the metal atoms in the outer shell dramatically change the electronic structure of the metallic aggregate, as the surface to volume ratio is very high. Moreover, the ligands prevent a strong interaction with the support, which is of crucial importance for the study of model catalysts.

An alternative strategy is the development of local spectroscopies that allow the spatial selection of single clusters on the support. At the present stage, the only available spectroscopy that presents enough sensitivity and spatial resolution for a single-cluster spectroscopy is the electron tunneling spectroscopy with a scanning tunneling microscope (STM). Scanning tunneling spectroscopy (STS) provides a three-dimensional real-space picture, which allows us to determine the size and the shape of the supported particle, and spectroscopic information on both filled and empty electronic states close to the Fermi level. The drawback is that it requires a conductive support presenting an atomically flat surface.

In this paper, we present a study with a STM in ultrahigh vacuum (UHV) of the size-dependent electronic structure of supported palladium clusters obtained by evaporation onto highly oriented pyrolitic graphite (HOPG). This system is usually regarded as a model catalyst to investigate the role of the cluster morphology and size in more conventional catalysts.[9,10] In particular, we study the surface density of states (DOS) at the Fermi energy, which plays a crucial role in the

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chemical properties of the cluster, and show how it dramatically depends on the cluster size. Other techniques (e.g., photoemission, microwave absorption, nuclear magnetic resonance, conduction electron spin resonance, surface plasma resonance[1]) have been applied to study the evolution of the whole electronic structure of supported, embedded, and free clusters; the electron tunneling spectroscopy permits us to investigate the electron density of states projected onto the *surface sites* of the clusters. This is the true electron density involved in the chemical reactions occurring at the surface of the metallic particles in supported catalysts. We show how the surface density of states builds up smoothly with increasing size and reaches a saturation value for a critical volume which characterizes the border between the mesoscopic regime and the bulk limit.

II. THEORY

The potential of the electron tunneling spectroscopy with a STM in the study of the metals has been widely demonstrated.[11–13] Considering the electron tunneling from a tip to a conductive sample within the framework of the Bardeen Hamiltonian,[12] the derivative of the tunneling current with respect to the tunneling voltage is proportional to the intrinsic surface density of states ρ of the sample,

$$\frac{dI}{dV} \propto \sum_{\nu} \delta(E_\nu - eV - E_F)|\Psi_\nu(\mathbf{r})|^2 \propto \rho(\mathbf{r}, E_F + eV), \tag{1}$$

where E_ν are the eigenvalues of the electronic Hamiltonian, Ψ_ν the electronic wave functions, and E_F the Fermi energy. This treatment is exact for a small bias V, which corresponds to tunneling electron states about the Fermi energy. Thus, the differential conductance at zero bias, that is the slope of the current-voltage curve for small voltages, provides information about the Fermi-level density of states (FLDOS) of the sample. The basic idea of this work is to compare the local FLDOS measured on equivalent sites of different clusters. The size, the shape, and the material of the tip influence the STM scan, as well as the measured electronic structure. Rigorously, the density of states that appears in Eq. (1) is the convolution of the DOS of the sample and that of the tip. However, as long as the tip does not change during the experiment (which can be verified by repeating the acquisition on the same cluster several times in different stages of the experiment), different tunneling conductances can be attributed to different densities of states of the clusters.

In a free-electron picture, the electronic structure of a microcrystal consists of a discrete set of energy levels, which approaches the quasicontinuous distribution of the bulk band structure as the size of the particle increases. For large clusters, according to the Kubo's criterion,[6] the density of states at the Fermi level is proportional to the number of atoms in the cluster. This behavior is a consequence of the surface potentials that remove the degenerations of the levels. Disregarding this effect, as in Frölich's picture,[14] the DOS would be proportional to the squared radius of the particle. The validity of Kubo's theory has been verified in the quasistatic conductivity of metal particle dispersion.[15]

In this paper, we show how the electronic structure of the surface evolves with size for single particles that are strongly interacting with a conductive surface (the graphite). In very small clusters the discretization of the levels should lead to oscillations in the tunneling probability as a function of the applied voltage. The resolution required to observe this effect is at least of the order of the level spacing. In the absence of other effects, the thermal broadening ($\simeq 2KT$) limits the resolution of the tunneling spectroscopy. At room temperature, the working temperature of our apparatus, the theoretical resolution is 50 meV. If we assume a simple picture of the clusters in terms of free electrons confined in a box, we obtain that the level spacing is larger than the resolution of the tunneling spectroscopy only for very small clusters (of the order of a few Å). By increasing the cluster size, even though the resolution does not allow the detection of the single levels, it is possible to observe how the DOS at the Fermi level builds up and reaches the limit of the bulk metal.

III. EXPERIMENT

Experiments were performed in an ultrahigh-vacuum chamber with a base pressure of 2×10^{-10} torr, equipped with a commercial STM (WA-Technology), AES (Auger electron spectroscopy), and low-energy electron diffraction systems and standard facilities for sample preparation and metal evaporation. The sample can be introduced in vacuum via a fast-entry lock and transferred by means of a magnetic arm to the manipulator and into the STM. HOPG clean surfaces were prepared by peeling off some carbon layers by means of adhesive tape, producing a clean, but not well ordered, polycrystalline surface. Peeled HOPG samples were annealed by direct resistive heating *in situ* up to 700 K. No impurities were detected by AES. Pd was deposited at a constant rate of about 0.1 ML/min (1 ML is defined as the number of the graphite surface atoms) onto the clean surface kept at about 300 K. The Pd coverage was estimated on the basis of AES measurements from the ratio between the Pd(MNN) and C(KLL) Auger transition at 330 eV and 272 eV, respectively, calculated from the same derivative spectrum, and scaled by the ratio of the relative sensitivity factors. The AES analysis does not reveal the presence of oxygen at the surface of the particles. Chemical etched tungsten tips were used for STM/STS measurements. Tips were then cleaned in vacuum by means of voltage pulses (up to 100 V), in order to obtain a stable even if not very sharp tip. Atomic resolution was obtained on graphite and the mean measured corrugation was about 0.5 Å. Current-to-voltage measurements (I/V curves) were taken under conditions of constant tip-sample distance.[16,17] The constant current approach was not suitable for our purpose, which was to measure the surface DOS at the Fermi level. The tip was positioned at a selected point of the surface, providing that the x, y piezodrift was negligible at least during the measurement. The feedback loop was then interrupted and the voltage increased in steps (256) in a specified range (−1 V,+1 V), while the corresponding values of the tunneling current were recorded. Averaging was often required to improve the signal-to-noise ratio. Several I/V curves were consequently recorded at a given sample point, provided that the feedback controller was reactivated after each voltage ramping, to recover the starting settling conditions.

IV. RESULTS AND DISCUSSION

Figure 1 shows a STM image of a typical distribution of Pd clusters obtained with our deposition technique. The clusters appear as islands of heights ranging from 5 Å to 20 Å with a rather broad lateral size distribution (from a few Å to tens of nm). When the deposition is performed on the hot support, the clusters migrate and decorate the steps of the graphite (see Fig. 2); this phenomenon does not occur when the deposition is performed at room temperature. The clusters bonding to the surface is strong enough not to be dislodged by the interaction with the tip during the scanning process. This was verified by collecting several consequent images of the same area. Atomic resolution was repeatedly obtained on the graphite, but not on the clusters, which exhibit a smaller surface charge corrugation (see Fig. 3). Decreasing the size of the scanned area, it was possible to isolate small groups of clusters of different sizes (see Fig. 4), and to acquire the current-voltage spectra; in order to test the reproducibility of the measurements, acquisitions were repeated after moving the tip away from the cluster. The tunneling current on the clusters turned out to be noisier than on the graphite, and signal averaging was necessary. Every spectrum was obtained adding 32 acquisitions. Strong oscillations in the transmission probability have been observed for a bias voltage larger than 1 V. These oscillations are incoherent and can be averaged off by adding several scans. The amplitude of these oscillations for voltages larger than 2 V can be as large as 80% of the measured current. Averaging 32 scans leads to a residual noise of about 10%. For an applied bias smaller than 1 V, strong oscillations are not observed, and a single scan gives a signal-to-noise ratio of about 5.

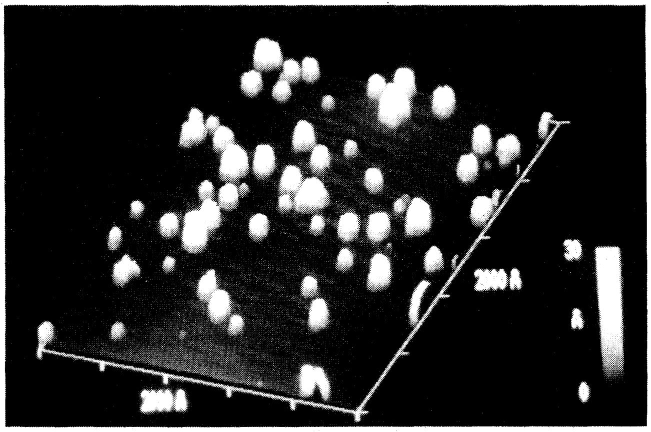

FIG. 1. STM image of palladium clusters on a flat area of the graphite. The size distribution of the particles is very broad, and clusters between 10 Å and several hundred Å can be seen.

When the surface of the clusters is covered with oxides that form a tunneling barrier between the metallic particle and the support, Coulomb blockade effects are usually observed.[18] In our case, the deposition was performed in UHV, and AES spectra confirm that the surface of the particles is clean from oxygen. Thus, we do not expect a barrier between the cluster and the substrate. Due to the different electronic structure of the cluster and of the graphite, however, different characteristic times for the electron tunneling to the cluster and the following passage to the support can introduce noise. This phenomenon might be responsible for the strong oscillations of the current-to-voltage characteristics for large applied voltages. Analogous oscillations occur when the bias is larger then the work function of the metal.[11] In our case, the evaluation of the image-charge contribution to the work function is not straightforward, because of the presence of a conductive substrate and the heterogeneity of the system cluster+support. Anyway, we should assume a "work function" (or more properly, in the case of a cluster, an ionization energy) for the particles much smaller than that of an infinite Pd surface [5.6 eV for the (111) face]. Thus, this latter mechanism seems less likely.

Figure 5 shows the derivative of the current-voltage characteristics at zero voltage as a function of the cluster volume. The experimental parameters (tip distance, feedback gain, etc.) were set constant in every acquisition. The derivative was determined by fitting the linear part of the current-voltage curve. Above a critical volume of the cluster the tunneling conductivity reaches a limiting value and becomes independent on the size. In Fig. 6 we report a magnification of the plot of Fig. 5 for clusters of small sizes. It is noticeable that for small clusters the surface FLDOS increases linearly with the volume. Deriving an absolute value for the density of states is not easy, as many unknown factors are involved, mainly details on the electronic structure of the tip and the exact distance of the tip from the sample. However, the effect of the size on the electronic structure of the surface is net. Similar effects have already been reported for colloidal dispersions,[15] free clusters,[19] and two-dimensional islands of divalent metal.[20,21] In the last case, it has been demonstrated that the metallicity of the clusters (detected by resonant photoemission) is determined by the average coordination number of the atoms in the particle.[21] The size-induced metal-insulator transition detected by Marquardt, Nimtz, and Mühlschlegel[15] in the quasistatic conductivity of small indium particles embedded in silicon oil, also seems to present close analogies to our case, even though the results are referred to the whole electronic structure of the clusters averaged over a broad ensemble of sizes. Our results are compat-

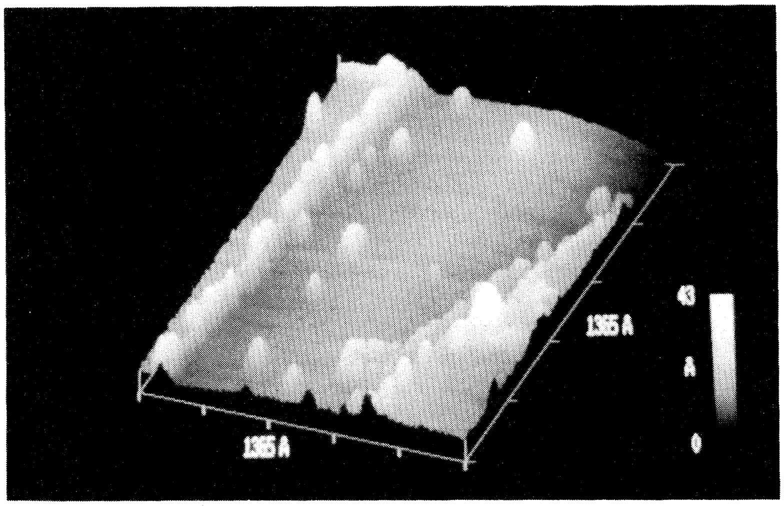

FIG. 2. Palladium clusters in the proximity of the steps of the graphite. When the metal is deposited on the hot support, the particles migrate and form rows along the steps.

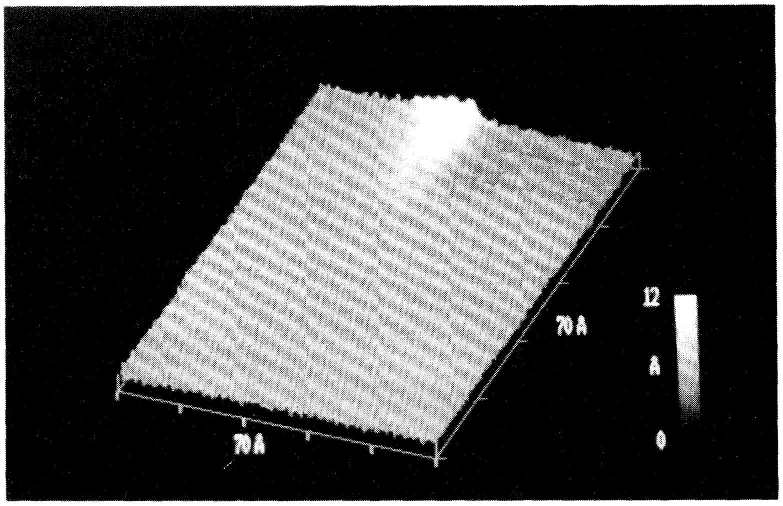

FIG. 3. A small-area STM image. The atomic resolution is achieved on the graphite. The cluster shows a vanishing electronic density spilling out of the surface which can be attributed to the evanescent states.

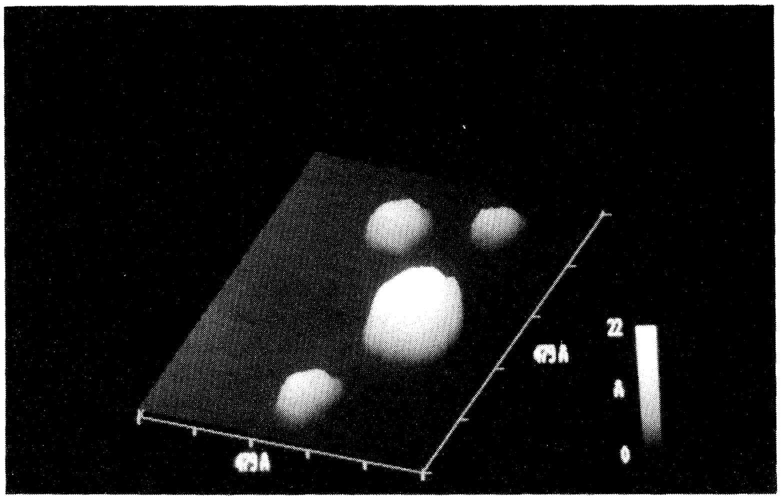

FIG. 4. Three clusters of different sizes in a small-area STM image. After spotting small groups of particles, it was possible to measure the I/V characteristics as a function of the size.

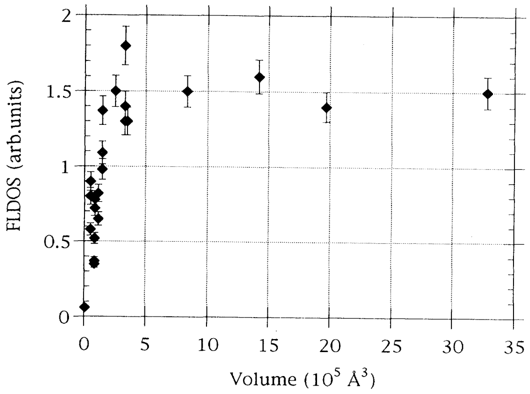

FIG. 5. Density of states at the Fermi energy as a function of the volume of the Pd clusters. Above a critical volume, the electronic structure of the surface becomes size independent.

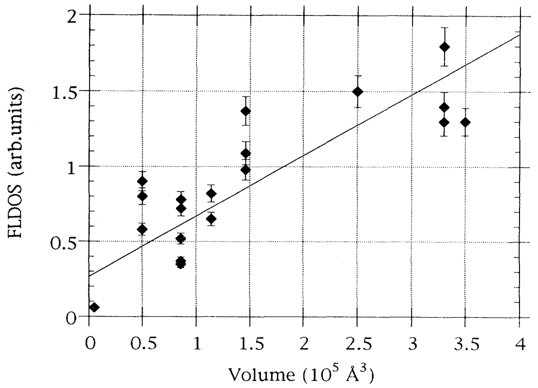

FIG. 6. Magnification of the plot of Fig. 5 in the region of small sizes. The density of states at the Fermi level increases linearly with the volume.

ible with Kubo's picture[6] of a discrete system of levels, the spacing of which is dependent on the volume of the cluster. Such a simple approach, however, does not take into account the interaction of the metal with the support which, in the present case, is strongly coupled with the cluster, as it works as a drain (or a source) for the tunneling electrons. The existence of a critical volume, above which the surface Fermi-level DOS does not change any more, indicates the incipient infinite surface electronic structure. In Ref. 22 the existence of this threshold is related to the Thouless coherence length of the conduction electrons which, when comparable to the size of the cluster, causes the discretization of the electronic structure. The critical volume observed in our particles is determined by the lateral extension of the metallic island, rather than from the height, the range of variation of which is much smaller. The estimated Thouless length for the electrons in our clusters turns out to be of the order of 100 Å, much smaller than the value reported in Ref. 15 for the indium particles (about 1 μm). In order to account for such a large value, Marquardt and Nimtz[22] have pointed out that, due to the finite size of the microcrystal, long wavelength acoustic phonons are not allowed, and the electron-phonon inelastic scattering is less effective. In the case of a strong interaction with the support, as in our case, we expect that the phonon branches of the particles mix with those of the support and that the inelastic diffusion is not so dramatically affected by the size.

In conclusion, we have reported the evolution of the surface DOS at the Fermi level for individual Pd particles supported on graphite. This is usually regarded as the physical quantity that determines the chemical properties of cluster-based heterogeneous catalysts. The observed gradual development of the density of states can be attributed to the incipient band structure. The present results reveal that the transition to a fully metallic behavior is not abrupt and that a strong parallel exists between the metal-nonmetal transition in supported particles and in free or embedded clusters.

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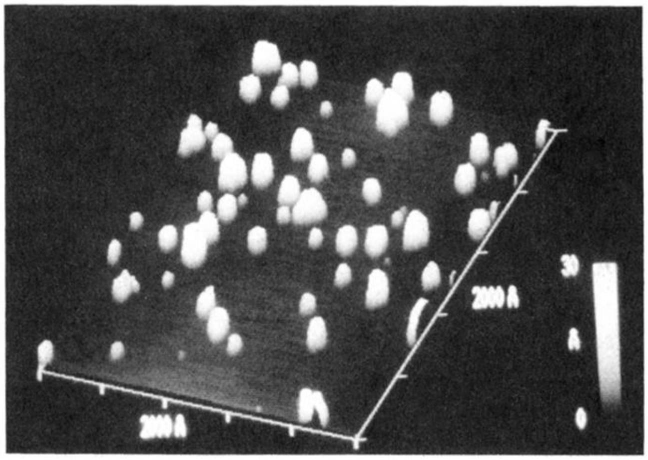

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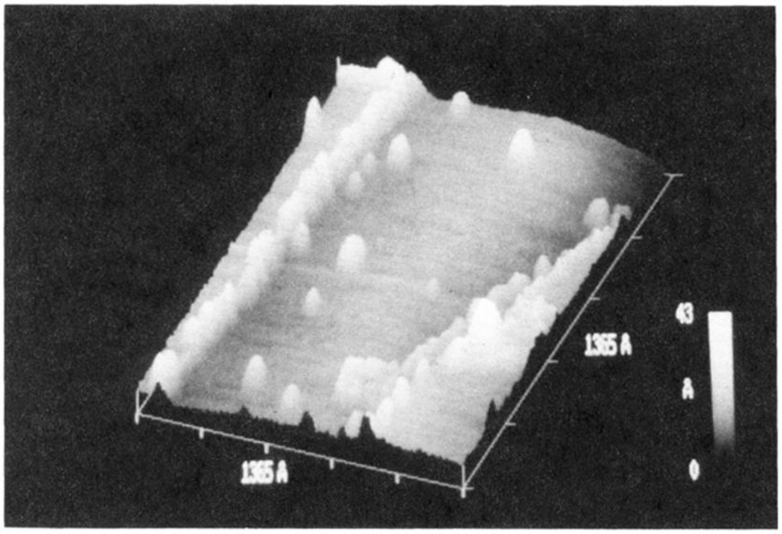

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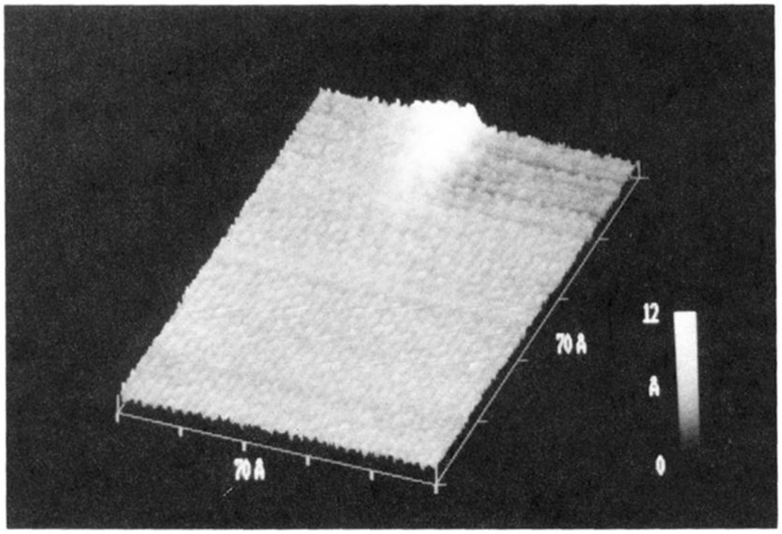

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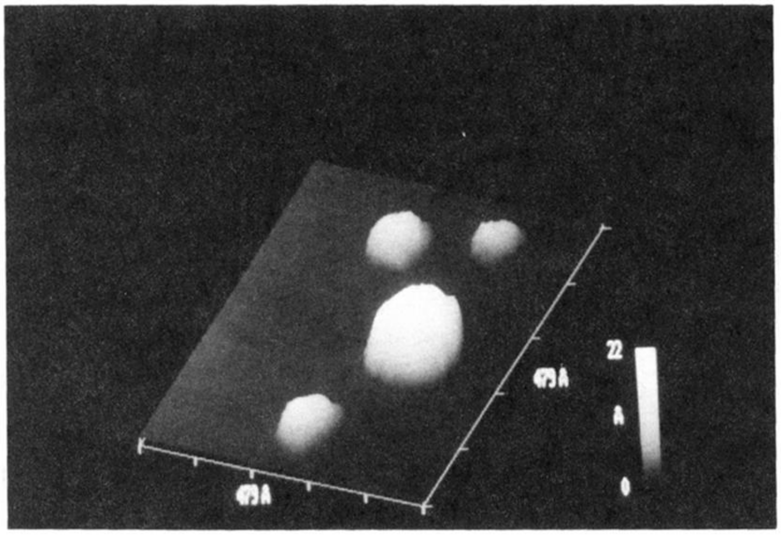

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